Pulsed Power Production of Ozone in O_2/N_2 in a Coaxial Reactor without Dielectric Layer

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ABSTRACT

Very short duration pulsed streamer discharges have been used to produce ozone in a gas mixture of nitrogen and oxygen at atmospheric pressure. The ratio of nitrogen to oxygen in the mixture was varied in the range from 2.5/0.5 to 0.5/2.5, while maintaining a total flow rate of 3 l/min. The production of ozone was found to be higher for a specific mixture ratio of N_2/O_2 than that in oxygen or in dry air. The production of ozone in O_2 was higher than that in dry air. The production yield of ozone (g/kWh) increased with decreasing nitrogen in the O_2/N_2 mixture. It has been found that the peak of the streamer discharge current decreased with time after application of the pulsed power. This decrease in the current corresponded with the increase in the ozone production and is attributed to the loss of electrons in the discharge current due to their attachment to ozone to form negative ions.

1 INTRODUCTION

NON-THERMAL plasma discharge, created by using very short duration pulsed power technology, is an effective method for ozone production. Ozone is resolved into harmless substances of oxygen and carbon dioxide in the presence of organic substances without objectionable byproducts or residues in the environment. Therefore a reliable and cost-effective generation of ozone will replace increasingly other chemical oxidants such as peroxides, permanganates, dichromates, chlorine and chlorine compounds, due to its better environmental compatibility as well as requiring a lower energy consumption for its production [1–4].

Pulsed power production of ozone offers substantial advantages over other methods in producing intense streamers [5]. These include a production of non-thermal plasma when very short pulses of $\sim$ 120 ns lengths are used, whereas the temperature of the gas remains near the ambient [6] and a breakdown of the gas leading to the formation of an arc does not readily occur [7, 8]. Plasma chemical processes using ozone have been known to be highly effective in promoting oxidation for a wide range of applications. These include treatment of waste water, processing of semiconductor devices, treatment of industrial wastes, bleaching processes, chemical synthesis and removal of NO_x and SO_x from flue gases [1–4]. The decay of ozone increases drastically with elevated temperatures [9, 10]. Because ozone is unstable it must be generated where it is required to be used [1–4].

It was reported previously that the ozone concentration in parts per million (ppm) and the production yield in g/kWh were higher in pure oxygen than in dry air [11]. The higher production in oxygen was more predominant at higher voltages. Therefore, it is of interest to investigate the production of ozone in mixtures of nitrogen and oxygen of different ratios, with the goal of of finding whether a particular ratio might lead to a higher production or a higher yield than for those in pure oxygen. In the present paper the concentration and the production yield of ozone were determined in nitrogen and oxygen mixtures over a wide range of ratios of the mixture, and also were compared to those in oxygen and in dry air. The flow rate ratios of N_2/O_2 covered were from 2.5/0.5 to 0.5/2.5, while the total flow rate was kept constant at 3 l/min, the pressure at 1.01×10^5 Pa and the temperature at 26±4℃.

2 EXPERIMENTAL PROCEDURE

In the coaxial reactor used for the generation of ozone, a discharge gap was formed between a spiral copper wire of 1 mm in diameter coiled on vinyl chloride tube [12, 13] having diameters of either 22 or 26 mm and a copper tube 58 mm in internal diameter. Thus, the gaseous gap between the electrodes was either 17 or 15 mm. Oxygen and nitrogen were obtained from gas cylinders having a purity of 99.50 and 99.99%, respectively. Dry air was obtained also from a gas cylinder. For gas mixtures of O_2 and N_2, the proportions of the mixtures were determined by controlling separately the flow rates of O_2 and N_2 in the range 0.5 to 2.5 l/min while keeping the total flow rate of the mixture constant at 3 l/min.

The concentration of ozone was monitored using an ultraviolet (UV) absorption ozone meter at 253.7 nm. The measurements were instantaneous and did not suffer from errors that may arise due to the presence

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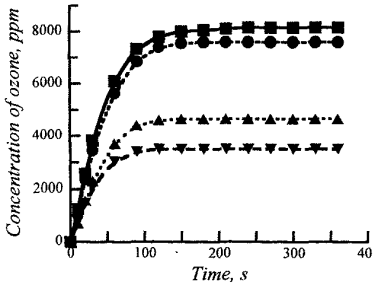

Figure 1. Concentration of ozone *vs.* time of application of pulsed power for different ratios of nitrogen and oxygen. Conditions: Peak pulsed voltage, 29 kV; pulse repetition rate, 100 pps; electrode gap, 15 mm; total flow rate, 3.0 l/min; N_2/O_2 flow rate ratios in l/min: ■ 0.5/2.5, ▲ 1/2, ● 2/1, ▼ 2.5/0.5.

of nitrogen oxides in the gas [1]. The gas mixture was admitted axially into the reactor at the required flow rate while the pulsed power was applied to the reactor. At least 150 s were allowed for the ozone production to reach a steady state as shown in Figure 1. The time it took for the production of ozone to reach a steady state was found to be independent of the ratio of N_2/O_2 in the mixture. All the results presented in this paper are for the saturated values of the ozone concentration. The pulsed voltage, the discharge current, the flow rates and the concentration of ozone were recorded continuously. The power was then turned off after ~ 5 min in the saturated condition. Various parameters such as the flow rates of the gases and the peak pulsed voltage were adjusted and then the same procedure was followed. The pulse repetition rate generally was fixed at 100 pps. The output gas from the ozonizer was exhausted to the outdoors through a charcoal trap.

A HV pulse was applied to the central electrode and was obtained from a magnetic pulse compressor (MPC), which can be operated at a variable pulse rate of up to 500 pps (pulses per second) and 62 kV peak voltage. A brief description and a circuit diagram of the MPC were reported recently [12]. A positive polarity pulse was applied to the central electrode because with this polarity the production of ozone was higher than that with the negative polarity [14, 15] due to more streamers and more branching per unit length of the wire [15, 16]. The output voltage and the discharge current were determined using a combination of a HV capacitive divider, a Rogowski coil and a calibrated digital oscilloscope (HP54542 A).

3 RESULTS AND DISCUSSION

Figure 1 shows the concentration of ozone as a function of time of application of energy into the reactor at a fixed applied pulsed voltage of 29 kV and varying N_2/O_2 flow rate ratios in the range 0.5/2.5 l/min to 2.5/0.5 l/min using a reactor with 15 mm gaseous gap. It will be observed that the concentration of O_3 steadily increased with time until saturation took place. Typically the saturation in the concentration of ozone occurred for times $\geqslant$ 150 s for all mixture ratios. Figure 1 shows that the concentration of O_3 increased at a fixed time with decreasing ratio of N_2/O_2 from 2.5/0.5 l/min to 0.5/2.5l/min. This is due to the increasing proportion of O_2 in the mixture, which resulted in a higher production of atomic oxygen, which is a prerequisite for the production of ozone.

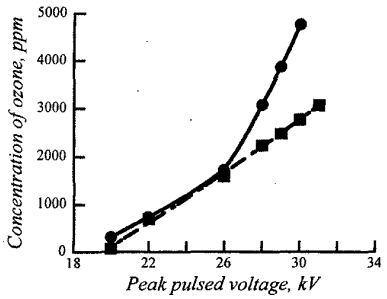

Figure 2. Dependence of the concentration of ozone *vs.* peak pulsed voltage in O_2 and in dry air. Conditions: gases ● oxygen, ■ dry air; flow rate 3.0 l/min; pulse repetition rate 100 pps; electrodes gap 17 mm.

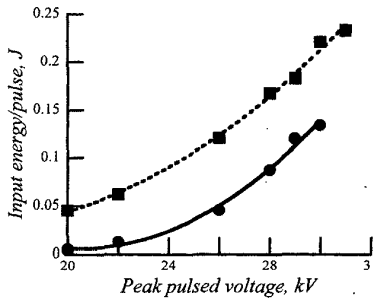

Figure 3. Figure 3. Dependence of the input energy per pulse into the discharge on peak pulsed voltage. Conditions and symbols as in Figure 2.

A comparison also is made of the performance of this reactor in pure oxygen and in dry air. It will be observed from Figure 2 that the concentration of ozone was higher for oxygen than for dry air throughout the voltage range used from 20 to 31 kV. After the applied pulsed voltage increased to >26 kV, the production of ozone was noticeably higher in oxygen than in dry air of up to ~ 71.8%, for the conditions depicted in Figure 2. The higher production of ozone in oxygen compared to dry air is due to the availability of larger concentration of oxygen in pure oxygen compared to that in dry air, with which electron collisions take place to produce the radical O and subsequent collisions with O_2 and a third body to produce O_3.

The higher production of O_3 in pure oxygen than in dry air is in general agreement with previously reported studies using other techniques [11]. The limit on the upper voltage level shown in Figure 2 was set by the onset of the breakdown of the gaseous gap leading to the formation of an arc and the subsequent collapse of the voltage. This was more likely to occur in this reactor as it had no dielectric barrier [17].

The input energy into the discharge per pulse is shown in Figure 3 for dry air and oxygen. It will be observed that the input energy (in J/pulse) into the discharge at a fixed pulsed voltage was higher in dry air than in oxygen, over the whole voltage range. This is because the

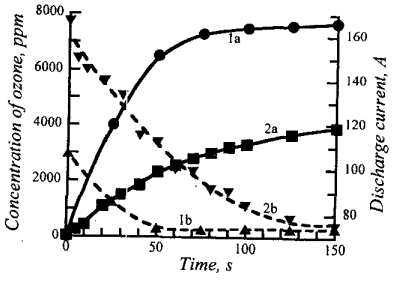

Figure 4. Dependence of concentration of ozone and peak discharge current on time in oxygen and in dry air. Conditions: peak pulsed voltage 36 kV; pulse repetition rate 150 pps; electrodes gap 17 mm; flow rate for either oxygen or dry air 2.0 l/min; curve 1a, concentration of ozone in oxygen; curve 1b, peak discharge current in oxygen; curve 2a, concentration of ozone in dry air; curve 2b, peak discharge current in dry air.

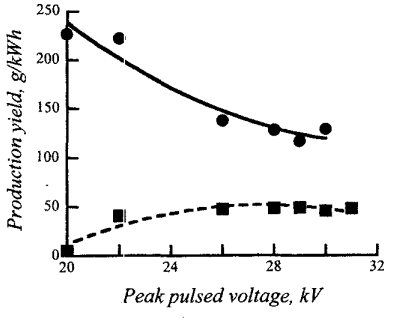

Figure 5. Dependence of the production yield of ozone on peak pulsed voltage. Conditions: gases ● oxygen, ■ dry air; flow rate 3.0 l/min; pulse repetition rate 100 pps; electrode gap 17 mm.

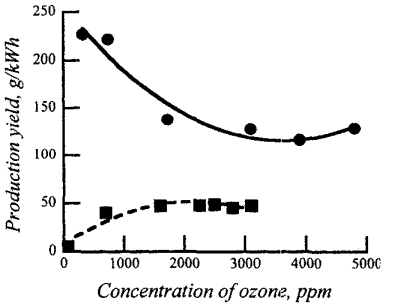

Figure 6. Dependence of the production yield of ozone on concentration of ozone. Conditions and symbols as in Figure 5.

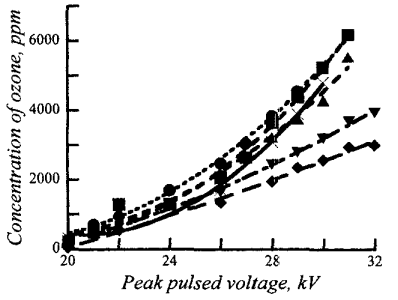

Figure 7. Concentration of ozone *vs.* pulsed voltage at different ratios of oxygen and nitrogen. Conditions: pulse repetition rate 100 pps; electrode gap 17 mm; total flow rate 3.0 l/min; N_2:O_2 flow rate ratios in l/min: × 0/3, ■ 0.5/2.5, ● 1/2, ▲ 1/1, ▼ 2/1, ♦ 2.5/0.5.

discharge current, for the same applied peak voltage, was much higher in dry air (Figure 4, curve 2b) than in oxygen (Figure 4, curve 1b), leading to a higher input energy into the discharge. The input energy per pulse steadily increased with increasing applied peak pulsed voltage in both oxygen and dry air (Figure 3).

Figure 4 shows that the peak discharge current is substantially higher (Figure 4,curve 2b) in dry air than in oxygen (Figure 4, curve 1b). This is because O_2 is an electronegative gas, which results in a reduction of the discharge current due to a stronger electron attachment than in dry air, and because the production of ozone is much higher in oxygen (Figure 4, curve 1a) than in dry air (Figure 4, curve 2a) leading to stronger electron attachment reactions and therefore a larger loss of electrons and consequently a lower discharge current (Figure 4, curve 1b). The peak discharge current decreased with time after application of the pulsed power by $\sim$ 54.7% in dry air (Figure 4, curve 2b) due to nitrogen oxide formation in addition to the production of ozone. In oxygen the discharge current diminished by $\sim$ 30.8% (Figure 4, curve 1b). It will be observed also from Figure 4 that the decrease in the discharge current corresponds to the increase in the concentration of ozone in the discharge reactor for both oxygen and dry air.

Figures 5 and 6 show the production yield η of ozone in g/kWh, calculated using Equation (1) in oxygen and in dry air as a function of pulsed voltage and concentration of ozone, respectively.

$$\eta = 3.6\times2.14\frac{FC(O_3)}{fE} \qquad (1)$$

where F is the flow rate (l/s), C is the concentration of ozone (ppm). 1 ppm of ozone in 1.01×10^5 Pa of air at 293 is equal to a density of 2.69×10^{19} mol/m^3 and to a mass density of 2.14 mg/m^3, f the pulse repetition rate (pulses/s) and E (J/pulse), the input energy to the reactor per pulse (the constants in Equation (1) are used to convert the units to g/kWh). It will be observed from Figure 5 that the production yield in oxygen is much higher than that for dry air due to a higher concentration of ozone (Figure 2) and a lower input energy in oxygen (Figure 3), leading to a net higher production yield of O_3, which is consistent with Equation (1). Figure 6 shows that the yield decreased with increasing concentration of ozone in pure oxygen from 226.8 g/kWh at 315 ppm to $\sim$ 128.9 g/kWh at 4810 ppm. On the other hand the yield was at a lower level in dry air. Typically it increased very modestly from 41 g/kWh at 700 ppm to 48 g/kWh at 3100 ppm (Figure 6).

Figure 7 shows the concentration of ozone as a function of applied pulsed voltage for different ratios of N_2 and O_2. It will be observed that the concentration of ozone increased with increasing pulsed voltage over the whole range covered during this study. It will be seen from Figure 7 that the flow rate ratios of N_2/O_2=1/2 to 0.5/2.5 l/min gave the highest concentrations of ozone over a wide range of pulsed

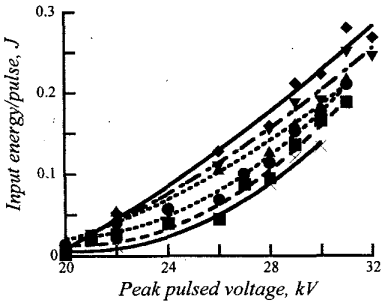

Figure 8. Input energy per pulse into the discharge *vs.* peak pulsed voltage at different ratios of oxygen and nitrogen. Conditions and symbols as in Figure 7.

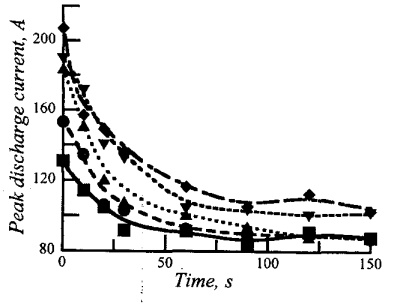

Figure 9. Dependence of peak discharge current on time at different ratios of oxygen and nitrogen. Conditions and symbols as in Figure 7.

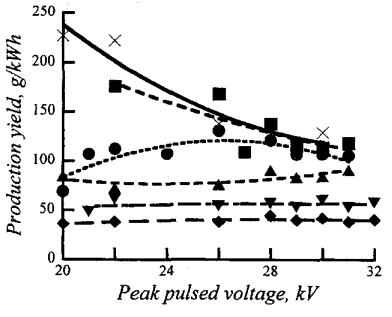

Figure 10. Production yield of ozone *vs.* peak pulsed voltage at different ratios of oxygen and nitrogen. Conditions and symbols as in Figure 7.

voltage. This was due to the high concentration of O_2 in the mixtures used. The ratio of N_2/O_2 of 2.5/0.5 l/min gave the lowest concentration of ozone due to the reduced concentration of O_2 in the gas mixture. It should be noted that the presence of a small amount of nitrogen led to a higher concentration of ozone than in pure O_2 (Figure 7). It is suggested that the additional amount of nitrogen modified the average electron energy, which led to more effective production of atomic oxygen, which is a prerequisite for the production of ozone. However, using a larger amount of nitrogen decomposed the already generated ozone due to nitrogen oxide formation, which is predominant at higher NO_x concentrations [9, 18].

Figure 8 shows the input energy/pulse against peak pulsed voltage for a wide range of ratios of N_2-O_2 mixtures. This shows that the input energy per pulse increased at a fixed applied voltage with decreasing proportion of O_2 in the mixture. This is due to the higher discharge current with decreasing O_2 in the mixture (Figure 9). As the proportion of O_2 in the mixture of N_2-O_2 decreases, the loss of electrons due to the electron attachment reaction also decreases. This leads to a larger discharge current in the gap as observed in Figure 9.

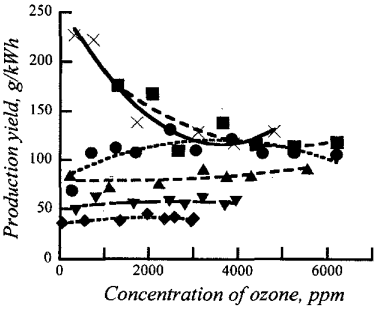

Figure 11. Dependence of production yield of ozone on its concentration at different ratios of oxygen and nitrogen. Conditions and symbols as in Figure 7.

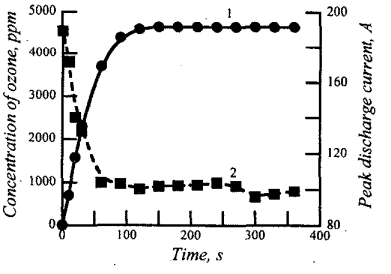

Figure 12. Dependence of ozone concentration and peak discharge current on time after applying a peak of the applied pulsed voltage of 29 kV at a flow rate ratio of N_2/O_2=2/1 l/min. Conditions: Total flow rate 3 l/min; pulse rate 100 pps; electrode gap 15 mm; curve 1, concentration of ozone; curve 2, peak discharge current

The production yield of ozone as a function of peak pulsed voltage is shown in Figure 10 for different flow rate ratios of N_2 and O_2. It will be seen that the production yield increased with increasing the proportion of O_2 in the mixture (Figure 10). This is due to the higher concentration of O_3 (Figure 7) and lower input energy into the discharge (Figure 8), at a fixed applied voltage with increasing proportion of O_2 in the mixture. The production yield *vs.* the concentration of O_3 for different flow rate ratios of N_2 and O_2 is shown in Figure 11. It will be observed that the highest production yield was obtained for pure O_2 at low concentration of O_3. For the mixtures, the lowest yield was obtained at the lowest concentration of O_2 in the mixture at the ratio of N_2/O_2=2.5/0.5 l/min (Figure 11). The mixture of N_2/O_2=0.5/2.5 l/min had the highest production yield over a wide range of O_3 concentrations (Figure 11).

Figure 12 shows the peak discharge current and the corresponding concentration of ozone in a mixture of N_2/O_2=2/1 as a function of time after applying a pulsed power. It will be observed that the peak of the discharge current steadily decreased with increasing time until it reached saturation after ~ 120 s. The sharp decrease in the peak discharge current corresponds to the sharp increase in the production of ozone to the saturation as shown in Figure 12. This is attributed to the loss of electrons forming negative ozone ions (O_3^-) by electron attachment, which increased with increasing production of O_3 (Figure 12). In Figure 7 it is shown that the concentration of O_3 increases with increasing O_2 in the mixture of C_2/N_2. In Figure 9 the discharge current is also found to decrease with increasing O_2 in the mixture. Therefore the discharge current decreases as the O_3 concentration increases, which is consistent with the measurements depicted in Figure 12.

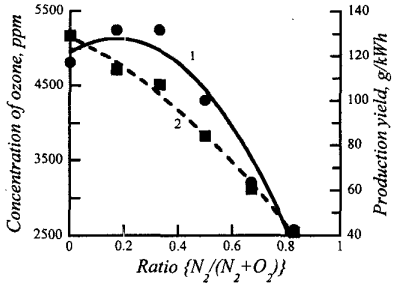

Figure 13. Dependence of concentration and yield of ozone on different ratios of N_2 and O_2 at 30 kV peak pulsed voltage. Curve 1, concentration of ozone; curve 2, production yield. Conditions as in Figure 7.

The dependence of the concentration of ozone and its yield (g/kWh) on the ratio of $N_2/(N_2+O_2)$ is shown in Figure 13. It will be seen that the production yield steadily decreased with increasing $N_2/(N_2+O_2)$ and therefore with decreasing O_2 concentration from 129.2 g/kWh in pure O_2 (N_2=0) to 41.6 g/kWh for $N_2/(N_2+O_2)$=0.8. This is because the decreasing proportion of oxygen reduced the concentration of ozone (Figure 7) and increased the input energy per pulse (Figure 8), resulting in lower production yield, which is also consistent with Equation (1). The concentration of ozone initially increased with increasing $N_2/(N_2+O_2)$ and then decreased when the ratio was above 0.33 (Figure 13) due to the same explanation suggested for Figure 7.

The concentration of ozone *vs.* the mixture ratio of $N_2/(N_2+O_2)$ is shown in Figure 14 for different peak pulsed voltages in the range 20 to 30 kV. It will be observed that for all mixture ratios from 0 to 0.83, the concentration of ozone was higher with increasing applied pulsed voltage. At a fixed ratio of about $N_2/(N_2+O_2)$=0.33, and for all pulsed voltages, generally the highest concentrations of ozone were obtained (Figure 14). Figure 15 shows the energy input/pulse into the discharge *vs.* the mixture ratio of $N_2/(N_2+O_2)$ for different applied voltages. The input energy/pulse into the discharge increased linearly with increasing ratio of $N_2/(N_2+O_2)$ at $\geqslant$ 26 kV. For voltage $\leqslant$ 22 kV, the input energy/pulse initially increased with increasing the mixture ratio and then reached saturation.

Chalmers *et al.* reported strongly dependent values of the yield on the pulse width from 300 g/kWh at 20 ns to 147 g/kWh at 120 ns, without a dielectric barrier, in oxygen [7, 19]. Masuda *et al.* [20] reported a yield of 170 g/kWh in oxygen using a surface discharge at 10 kHz with a high level of ozone production of 5 to 10%. Pietsch *et al.* reported yield values of 122 and 27.07 g/kWh in O_2 and in air, respectively using dielectric barrier discharges [21]. In commercial systems the production yield of ozone in air was reported to be 50 to 55.6 g/kWh (18 to 20 kWh/kg) [11]. Masuda *et al.* [20] reported in dry air that the yield values varied from 100.6 to 106 g/kWh in dry air using cylindrical ozonizers without a dielectric barrier. 77.4 to 200 g/kWh were reported using strip plates with dielectric barriers by Masuda *et al.* [15]. The results presented in the present work using pulsed power (Figures 5, 6, 10 and 11) compare favorably with the previously reported values of the production yield of ozone in dry air of $\leqslant$ 56 g/kWh (Figures 5 and 6) and in oxygen of up to 226.8 g/kWh (Figures 5 and 6).

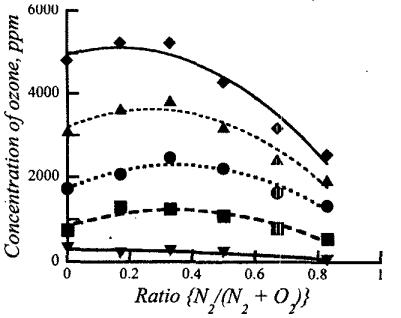

Figure 14. Concentration of ozone *vs.* different ratios of nitrogen and oxygen at various pulsed voltages.

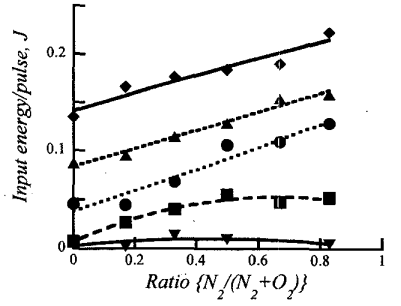

Figure 15. Dependence of input energy per pulse on different ratios of nitrogen and oxygen at various pulsed voltages. Conditions and symbols as in Figure 14.

4 CONCLUSIONS

1. In N_2/O_2 mixtures, the concentration of ozone increased with increasing applied peak pulsed voltage.
2. The concentration of ozone was highest for mixture ratios of N_2/O_2 of 1/2 l/min to 0.5/2.5 l/min. In this range the concentration of ozone was higher than for pure oxygen.
3. The input energy per pulse increased with increasing concentration of nitrogen in the N_2/O_2 mixture.
4. The production yield of ozone (g/kWh) increased with decreasing nitrogen in the N_2/O_2 mixture.

5. The input energy/pulse at a fixed mixture ratio increased with increasing applied peak pulsed voltage.
6. The reduction in the discharge current with time corresponded with increased ozone concentration in pure oxygen, in dry air and in N_2/O_2 mixtures.

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